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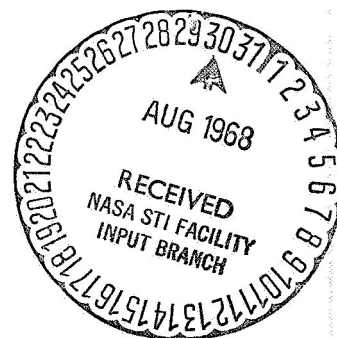
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OF CARBON-GRAPHITE MATERIALS

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ABSTRACT. The features of the interaction of synthetics graphites with oxidizing agents are examined and a method for isolating the effect of the physical and chemical factors is proposed. Experimental data on the differentiated determination of the loss rate of a graphite mass during oxidation by atmospheric oxygen are given.

/438[1]

Synthetic graphites are widely used in industry, although insufficient resistance to oxidation limits their range of application. The increasing importance of synthetic graphites in new areas of technology has resulted in the appearance of many works on the subject of the interaction of graphite with oxidizing agents [1, 2]. Unfortunately, many studies on the kinetics and mechanism of oxidation reactions completely ignore the structural features of synthetic graphites which are predetermined by the technology of their production, even though the effect of the micro- and macrostructure of graphite on its interaction with oxidizing agents is indisputable [3].

Synthetic graphites are produced by bonding a coke filler with coke formed during the carbonization of coal pitch, which is used as the binder, with the subsequent graphitization of the intermediate product [4], in such a way that the coke residue of the binder is not distributed uniformly around the particles of the filler, but forms bridge bonds between them [5]. The interaction of synthetic graphites with oxidizing agents occurs primarily by way of the oxidation of the binding bridges [6], which results in the disintergration of the unoxidized particles of the filler and an increase in the actual reaction surface.

In our work we have attempted to make a separate determination of the effects of physical and chemical factors on the mass loss rate of synthetic graphites during their interaction with oxidizers.

The schematic diagram of the experimental apparatus is shown in Figure 1. The test sample 11, having the form of a hollow cylinder with the dimensions (20 × 16) × 110 millimeters, is placed in heater 8 of silicone graphite. The sample is heated and cooled in vacuum chamber 4 under vacuum created by a VN - 1 mg vacuum pump. The temperature is measured by thermocouple 13 or by an OPPIR-017 optical pyrometer through viewing window 9. The oxidizing agent is admitted into the reaction chamber through rotameter 2. The desired pressure, controlled by manovacuometer 7, is established in the vacuum chamber by throttle valve 6. The power source of the apparatus consists of an OSU-40 power

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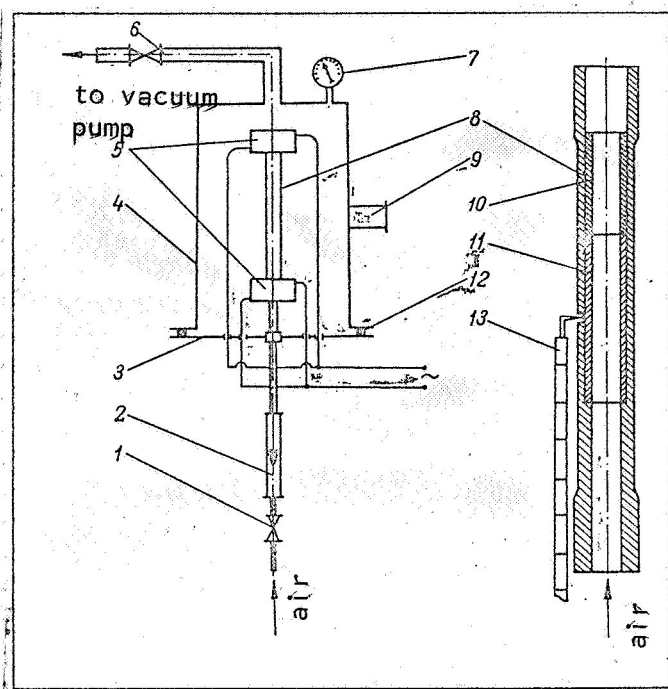[1] Numbers in the margin indicate pagination in the foreign test.

Figure 1. Schematic Diagram of Experimental Apparatus: 1,6- Valve; 2- Rotameter; 3- Tray; 4- Vacuum Chamber; 5- Current Supply; 7- Manovacuometer; 8- Heater; 9- Viewing Window; 10- Protective Insert; 11- Sample; 12- Packing; 13- Thermocouple.

transformer and two ROT-25/05 autotransformers. This apparatus makes it possible to carry out tests to an accuracy of ± 10% through a wide pressure range ($\leq$ atmospheric pressure) and in /439 a temperature range of 600-2000°C. We oxidized the graphite during our investigation at atmospheric pressure in an airstream with a velocity of about 0.02 m/sec.

For our investigation we selected three types of synthetic graphite, differing in the granulometric composition of the filler and in density.

During oxidation of the mechanically processed surface, which is an essential condition for the present method of determining the rate of oxidation of synthetic graphite, W reaches a constant value after a given time interval (Figure 2). The test graphites were oxidized at the temperature at which oxidation transitions from the tic to the extradiffusion zone. Under the conditions of our experiment this temperature was about 900°C. The preparation of the surface of the sample by oxidation at low temperatures is not desirable, since the durability of the graphite is substantially reduced [7] as a result of the oxidation of the binding bridges between the particles of the filler during intraporous reaction. Figure 2 shows that the time required for reaching the stationary condition of oxidation is directly proportional to the density of the graphite and the coarseness of its filler, while the value W = constant is inversely proportional to the same parameters. It should be noted that the force effect of the oxidizing agent on the reaction surface is insignificant in the given case. During the interaction of synthetic graphites with a gas stream flowing at a rapid rate onto the protruding grains of the filler, aerodynamic forces occur [8] which can change the nature of the dependence of W on the structural characteristics of the graphite.

We see in Figure 3 that the function $W = f(T)$ in the Arrhenius coordinate system has a rectilinear nature in the extrakinetic zone. This function is often used for determining the kinetic properties of the reaction of graphite with oxidizing agents [1, 2]. At the same time, the total mass loss rate of
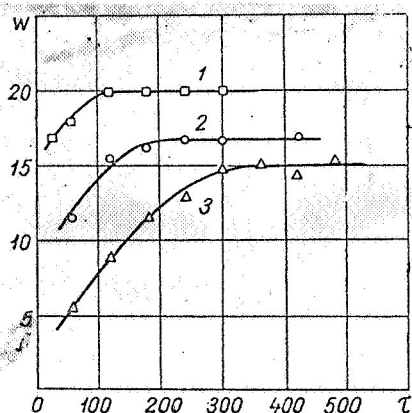
Figure 2. Effect of Oxidation Time By Atmospheric Oxygen on the Mass Loss Rate of Graphite (τ, sec, $W \cdot 10^3$, kg/m^2 $\cdot$ sec: 1) coarseness of filler -0.15 + 0 millimeter, density $\sim 1.65 \cdot 10^3$ kg/m^3; 2) -1.2 + 0 and $\sim 1.65 \cdot 10^3$; 3) -1.2 + 0 and $\sim 1.85 \cdot 10^3$.

graphite during oxidation can be represented by the expression

$$W = W_1 + W_2 + W_3, \tag{1}$$

where W_2 is determined by the total surface of the pores accessible to the oxidizing agent and W_3 depends, as shown in Figure 2, on the granulometric composition of the filler and the density of the graphite, i.e. these two components of W characterize the structure of synthetic graphites, but not the chemical properties of the graphite. This condition is apparently the main cause of the extremely contradictory results of kinetic investigations of the reactions of graphite with oxidizing agents which have been been conducted on samples of various brands of synthetic graphite.

The determination of the kinetic characteristics of the chemical reaction of graphite with oxidizing agents on the basis of the mass loss rate of carbon-graphite material during oxidation should obviously be recognized as unfounded on the basis of the above statements. The determination of the actual apparent activation energy of the chemical reaction of carbon and graphite with oxidizing agents is of great scientific and practical interest.

It follows from expression (1) that if $W_2 = 0$ and $W_3 = 0$, then $W = W_1$. This condition is satisfied by the oxidation of graphite not containing a filler whose grains are bridge-bonded, except for in the intrakinetic mode of oxidation. The latter is possible when the graphite does not have open porosity. <u>/441</u> Pyrographite [9] satisfies these prerequisites. It is practically impermeable to gas [10] and is monolithic, having a density which closely approximates the theoretical density.

The chemical reaction rate of graphite having crystals of randum orientation, which is characteristic of synthetic graphites produced by the methods of electrode technology, is defined as the arithmetic mean of the chemical reaction rates of graphite in the various crystalographic directions and can be represented as

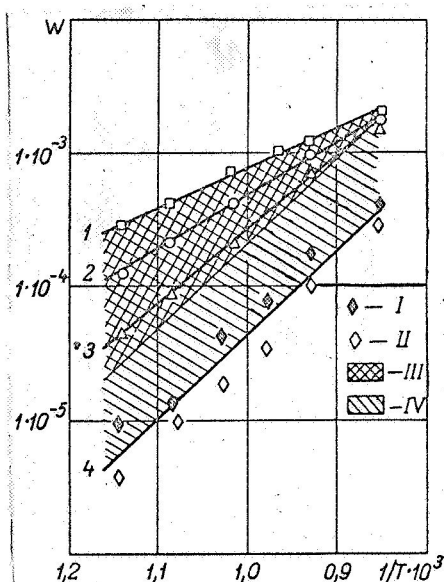$$W_1 = 1,5 \cdot 10^2 \exp\left(-\frac{29500}{RT}\right). \tag{2}$$

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Figure 3. Effect of Temperature on the Mass Loss Rate of Graphite During Oxida- by Atmospheric Oxygen ($\frac{1}{T} \cdot 10^3$, °K^{-1}; W, kg/m$^2 \cdot$ sec): 1, 2, 3) total mass loss rate of graphite (coarseness of filler -0.15 + 0 mm, density $\approx$ 1.65 $\cdot$ 10^3 kg/m^3; -1.2 + 0 and ~1.65 $\cdot$ 10^3; -1.2 + 0 and ~ 1.85 $\cdot$ 10^3, respectively); 4) rate of chemical reaction of graphite; I - rate of chemical reaction of crystal- oriented graphite along axis a; II - likewise along axis c; III - mass loss rate due to intraporous reaction; IV - increase in mass loss rate due to dis- integration of unoxidized filler parti- cles and increase in actual reaction surface.

The number of micropores whose surface, according to [11], is inaccessible to the oxidizing agent, is very difficult to es- tablish to the required accuracy during the experimental determina- tion of W_2. The direct experi- mental determination of W_3 is also very difficult.

We will show how it is possi- ble to determine W_2 and W_3 analy- tically on the basis of the ex- perimental data of W and W_1.

Above a given temperature W is limited by the feed rate of the oxidizing agent. Conse- quently the reagent begins to interact with graphite only on the outer surface and does not diffuse into the pores. It follows from expression (1) that when $W_2 = 0$,

$$W_3 = W - W_1.$$

(3)

The value of W_3 depends on the exposure rate of the filler par- ticles, determined by W_1, granu- lometric composition of the filler, and density, which are constant for a given brand of graphite. Therefore, the func- tion $\ln W_3 = f(1/T)$ can be represented as a straight line drawn from the point of transi- tion of oxidation from the extra- kinetic to the extradiffusion zone parallel to the straight line of the function $\ln W_1 = f(1/T)$.

In the extrakinetic reaction zone the amount of oxidizing agent is greater than the stoichiometric value. Consequently the surplus oxidizing agent diffuses into the pores of the graphite. In accordance with expression (1),

$$W_2 = W - (W_1 + W_3).$$

(4)

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We see from Figure 3 that at low temperatures the main component of the mass loss rate of synthetic graphites is intraporous reaction. As the temperature increases, mass loss occurs primarily by way of the disintegration of the unoxidized filler particles. The granulometric composition of the filler and the density of the graphite have only an insignificant effect on the amount of mass loss due to the disintegration of the particles (Figure 2) in comparison with their effect on the mass loss of graphite due to intraporous reaction. For a given granulometric composition of the filler, the proportion of intraporous reaction to the total mass loss of graphite is greater when the graphite is less dense, but for a given density, it is greater for graphite having a fine-grain filler.

Symbols.

W, total mass loss rate, $kg/m^2 \cdot sec$; W_1, chemical reaction rate, $kg/m^2 \cdot sec$; W_2, intraporous reaction rate, relative to unit external surface, $kg/m^2 \cdot sec$; W_3, increase in the mass loss rate due to the disintegration of unoxidized filler particles and an increase in the actual reaction surface, $kg/m^2 \cdot sec$; τ - oxidation time, sec; T, temperature, °K; R, universal gas constant, cal/deg $\cdot$ mol.

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